

PROCESS FOR PRODUCING COLORANTS

## BACKGROUND OF THE INVENTION

### (1) Field of the Invention

The present invention relates to colorants used in the IT-related machines and instruments.

5 More particularly, the present invention relates to colorants for color inks for use in the inkjet type printers utilizing the Piezo effect, bubble-jet type printers, etc. which are required to have a low viscosity and especially a low viscosity at  
10 high temperatures.

### (2) Description of the Related Art

As the colorant of the color inks for use in the inkjet type printers, oily inks constituted of an oil-soluble coloring matter substance and an organic  
15 solvent were used at first. Recently, however, water-based inks containing a water-soluble coloring matter substance have been developed according to the needs of making inks aqueous, and are used prevailingly.

However, water-based inks containing a water-  
20 soluble coloring matter substance are apt to undergo photo-degradation of the color in printed matter, because the coloring matter substances used therein are low in durability to light. As is well known, the use of pigments having higher light-durability as the

coloring matter substance is drawing attentions and a practical use of such pigments is being set forward.

Unlike soluble coloring matter substances that are present as molecules in a medium, the pigments  
5 as the coloring matter substance take a state of particles in a medium. Accordingly, the conversion from soluble coloring matter substance to pigments would have not become possible without the development of a dispersing technique of making the particle  
10 diameter of the pigment small to such an extent that the state of dispersion can be approximated to that in a solution. This fact is also known in the art.

It is well known that, regardless of the mode of the machine to be used, the inks for inkjet are  
15 essentially associated with a technique of transferring a liquid ink containing a chemical substance through a capillary at a high speed. Accordingly, one of the factors controlling the conditions of color is the chemical structure of a coloring matter substance in  
20 use. If this factor is excepted, the physico-chemical conditions which the liquid ink must satisfy are viscosity and those derived from the temperature dependency of viscosity. Specifically, said conditions include the viscosity of a medium, which controls the  
25 viscosity of the system, and the spatial size of the dissolved or dispersed solute, and the concentration and the temperature-dependence thereof.

The developmental efforts promoted from this

point of view is to simultaneously develop a method for dispersing a coloring matter substance into fine particles, and a dispersant that aids the dispersion of a coloring matter substance, which cannot disperse by  
5 itself into fine particles, without increasing the viscosity of the system, as an essential ingredient. The examples thereof include a combination of mechanical and chemical dispersing forces (JP-A-2000-119571), a method for chemical production of fine  
10 particle dispersion (JP-A-10-298294, JP-A-2000-119141, and JP-A-316242), a technique relating to an amphoteric resin having a dispersing performance (JP-A-2000-026560), etc.

On the other hand, regarding the improvement  
15 of a colorant containing a water-soluble coloring matter substance which takes advantage of the water-solubility, a combination of a water-soluble coloring matter substance and an amino acid, which is an amphoteric electrolyte, or the like (JP-A-2001-139854,  
20 JP-A-2000-136335, JP-A-9-12944, and JP-A-7-228816) can be referred to.

Further, an attempt to improve the water-resistance of a water-soluble dye type coloring matter substance by combining an oily dye type coloring matter  
25 substance, in place of a pigment, with a water-soluble resin dispersant (JP-A-2002-249689 and JP-2002-249687) is also reported.

As above, the development of inkjet inks for

making the most of the characteristic features of a coloring matter substance according to the properties of the coloring matter is ceaselessly continued at the present time. Nevertheless, the study has not yet  
5 reached the completion of the development, namely the provision of an ink capable of sufficiently fulfilling the required quality.

Reviewing the actual situation, the following can be pointed out. Thus, though pigment type inks are  
10 advantageous in terms of durability, they require pulverization into fine particles, thus the use of a high performance, expensive dispersing machine for the manufacture. Further, they require a polymeric dispersant which limits the lowering of viscosity and,  
15 as a result, the instruments in which such a ink is suitably usable are also limited (selectivity of instruments).

The method of using an oily dye type coloring matter substance as an aqueous dispersion is not so  
20 greatly different from the above-mentioned pigment system, because it requires a dispersing machine and uses a dispersant.

Although the method of improving the light-durability of a water-soluble water-based dye is epoch-  
25 making, this method seems to remain unreliable as it essentially uses an photo-degradable coloring matter substance and requires a photodegradation-inhibiting agent.

## SUMMARY OF THE INVENTION

As above, all the conventional colorants are meritorious in some point, but they are de-meritorious in some other point. Thus, it has been waited for to  
5 develop an colorant for inkjet inks that can overcome the above-mentioned problems of the conventional colorants and is free of the selectivity of instrument, high in the light-durability, high in reliability and inexpensive.

10 Accordingly, it is an object of the present invention to provide the above-mentioned "colorant for inkjet inks that is free of the selectivity of instrument, high in light-durability, high in reliability and inexpensive" by using chemical and  
15 physical means.

With the aim of solving the above-mentioned problem, the present inventors have conducted extensive studies. As a result, the present invention has been achieved by the technical means described below.

20 In the first place, the inventors studied on how the degradation of coloring matter substance by light takes place. As a result, the mechanism of the photo-degradation could be comprehended to some extent.

Concretely speaking, the photo-degradation  
25 reaction of water-soluble dyes was analyzed and found out to involve the changes of the color density, i.e. the absorbance, of the dye upon exposure to light in an accelerating manner with time, or to progress as if it

were an "autocatalytic" reaction as in chemical reactions, in other words. It was found reasonable to understand that the degradation progresses in such a manner that once coloring matter molecules undergo  
5 photo-degradation into the degradation product, the said degradation product then make adjacent normal coloring matter molecules degrade. It was actually ascertained that a coloring matter substance present in a membrane shows a greater extent of photo-  
10 deterioration than the same coloring matter substance present in a solution.

In the second place, the inventors thought about what coloring matter substance should be selected for satisfying the object of the present invention. As  
15 a result, there was arrived at a conclusion that since a water-soluble coloring matter, unlike an oil-soluble coloring matter, is imparted with an additional function of water-solubility, an oil-soluble coloring matter is considered to have higher chemical stability  
20 than a water-soluble coloring matter, and thus is preferable.

In the third place, the problem of aggregation was thought about. Thus, whether it belongs to a dye or a pigment, a coloring matter  
25 substance forms aggregates or associated matter, around an impurity electrolyte as a nucleus. It was found that such aggregates or associated matter can be broken down by applying an ion-exchange technique, whether the

medium is water or an organic solvent.

In the fourth place, there was a problem that, when a solution of an oil-soluble coloring matter in an organic solvent is used, it is desirable to  
5 convert the organic medium to an aqueous medium (phase conversion). The inventors found that this phase conversion can be easily carried out by bringing a coloring matter substance into a state of being solubilized as completely as possible, breaking down  
10 the fraction of the substance still remaining in the state of aggregates or association by an ion exchange technique and, while maintaining the solution in the above-mentioned state, portion-wise dropping the solution into an aqueous phase in which an amphoteric  
15 substance is dissolved. This is probably due to a fact that the amphoteric substance has an effect of stabilizing an electrolyte impurity by acting as a group opposite to the impurity that are apt to make the coloring matter substance re-aggregate after the phase  
20 conversion, regardless whether the impurity is an acid or a base (US Patent 3,652,478).

Further, in the colorant of the present invention, it is an essential condition that the coloring matter substance is a fine-particulate  
25 substance, so that, needless to say, the coarse particles which may exist unwillingly have to be removed.

Thus, according to one aspect, the present



invention provides a process for producing a colorant comprising a hydrophobic coloring matter substance, an amphoteric electrolyte and water, which comprises:

dissolving a hydrophobic coloring matter  
5 substance in an organic solvent miscible with water to obtain a coloring matter substance solution in which the concentration of the hydrophobic coloring matter substance is in the range of 1-10 wt%;

contacting the coloring matter substance  
10 solution with an anion exchange resin and/or a cation exchange resin to obtain a purified coloring matter substance solution;

adding dropwise, while stirring, the purified coloring matter substance solution into a solution  
15 containing an amphoteric electrolyte in de-ionized water at a concentration of 10 wt% or less to obtain a water-containing organic solvent solution of the purified coloring matter substance; and

removing the organic solvent from the water-  
20 containing organic solvent of the purified coloring matter substance by an azeotropic distillation of water and the organic solvent, while supplying de-ionized water and/or an organic solvent if necessary, optionally under an ambient or a reduced pressure to  
25 obtain an aqueous solution of the coloring matter substance and amphoteric electrolyte.

Further, according to another aspect, the present invention provides the above-mentioned process

wherein said solution of amphoteric electrolyte in de-ionized water is an aqueous solution of the coloring matter substance and amphoteric electrolyte obtained by a step of removing the organic solvent fraction by an  
5 azeotropic distillation or a step of high-speed centrifugation thereafter.

#### PREFERRED EMBODIMENT OF THE INVENTION

The embodiments of the present invention will be described below in more detail.

10 In the present specification, the steps included in the process of the present invention are called "Steps 1 to 5". However, the numbering used herein is only for the purpose of clarification, and it does not restrict the order of carrying out the steps.  
15 An embodiment of using a product of Step 4 or Step 5 in Step 3 also falls within the spirit and scope of the present invention, as mentioned in the description given below.

The process for producing a colorant of the  
20 present invention characterized by superiority in light-durability of hydrophobic coloring matter and stability of aqueous solution includes a step of dissolving a powdery hydrophobic coloring matter substance in a water-miscible organic solvent (Step 1).

25 The hydrophobic coloring matter substance used in the process of the present invention is preferably in a powdery form. In the present

invention, an oil-soluble dye is mainly supposed as the hydrophobic coloring matter substance. The oil-soluble dyes usable in the present invention include SY146, SY88, SY25, SY89, SY79, SY83-1, SY83, SY62, SY79, SY32, 5 SY19, SY81, SY82, SR130, SR233, SR125, SR122, SR127, SR92, SR124, SR89, SR8, SR91, SR109, SR119, SR160, SR118, SR132, SR218, SB136, SB45, SB44, SB70, SB38, etc. as indicated by C. I. No.

In the present invention, a pigment can be 10 also used as the hydrophobic coloring matter substance. The color of a pigment depends on the chemical structure of the pigment. The resistance to an organic solvent of a pigment is also governed by its chemical structure and varies. Accordingly, it is needless to 15 say that a pigment can be used in the present invention so far as its resistance to an organic solvent is not high, as it can be dispersed in a similar manner to the manner in which an oil-soluble dye disperses. Further, some pigments, depending on their chemical structures, 20 can be dispersed into an organic solvent to have a dissolved state close to that of oil-soluble dyes, by simply mixing the pigments with the organic solvent. Such pigments are also usable in the process of the present invention.

25 The organic solvent used in this step is not particularly limited, so far as it can dissolve a hydrophobic coloring matter substance well and is miscible with water because in the subsequent step it

is to be added dropwise into and thus diluted with an aqueous solution of an amphoteric electrolyte (e.g. an amino acid). The organic solvents which can be used include isopropyl alcohol, ethyl alcohol, methanol, 5 acetone, tetrahydrofuran, ethylene glycol, monoalkyl ether derivatives of ethylene glycol, propylene glycol, monoalkyl ether derivatives of propylene glycol, glycerin, diethylene glycol, alkyl ether derivatives of diethylene glycol, and the combination thereof. Of 10 these organic solvents, particularly preferable is isopropyl alcohol.

In this step, a coloring matter substance can be dissolved in the above-mentioned organic solvent according to the methods known to a person skilled in 15 the art, by using a dissolving tank equipped with, for example, a heating device, a reflux condenser, and a stirrer, etc. and by stirring the system, if desired.

Next, the step of purifying the solution of coloring matter substance obtained above (Step 2) will 20 be explained.

In the present invention, purification is carried out by subjecting the solution of coloring matter substance obtained above to an ion exchange treatment. As the method of ion exchange, those known 25 to a person skilled in the art, such as contacting the solution with an ion exchange resin by the use of an ion exchange tower, etc. can be referred to. Preferably, it can be carried out by adding an anion

exchange resin previously activated into the OH form and/or a cation exchange resin previously activated into the H form, which has been pulverized so as to have a particle size distribution between 10  $\mu\text{m}$  and 5 1,000  $\mu\text{m}$  and optionally dried, to the solution of coloring matter substance obtained above in an amount of 0.1-10 wt%, followed by agitation and the removal of the powdery ion exchange resin.

In the case where both the cation-exchange and anion-exchange are carried out, it is allowable to 10 carry out the cation exchange first and subsequently carry out the anion exchange after the removal of the cation exchange resin used. Otherwise, it is also possible to add the two types of powdery exchange 15 resins simultaneously and agitate the system to carry out both the cation-exchange and the anion-exchange. Further, it is also allowable to repeat the two ion exchange treatments alternately. The ion exchange using an ion exchange resin powder brings about an 20 equal ion exchanging effect whether the medium is an organic solvent or water.

The ion exchange resin that can be used in this step may be any of strong base-type anion exchange resins, weak base-type anion exchange resins, strong 25 acid-type cation exchange resins and weak acid-type cation exchange resins. The structure of the ion exchange resin is not particularly limited. That is to say, the resins may be any of porous type and gel type.

Principally, the type of ion exchange resin and the structure thereof should be selected in consideration of the properties of the target electrolyte and the pH value of the dispersion. Preferable ion exchange

5 resins are DIAION SA-20A and DIAION WK-10 which are a strong base-type anion exchange resin and a weak acid-type cation exchange resin, respectively, since they generally work well when used in a usual manner.

As the time period of the ion exchange, 30  
10 minutes or longer is enough for the purpose.

For powdering an ion exchange resin, a ball mill, a mortar type pulverizing machine, and a stone mill type pulverizing machine can be used.

For removing the resin powder from the  
15 solution of a coloring matter substance after the ion exchange, a method of filtration under an elevated pressure using a filter material capable of capturing the particles in the perpendicular direction with respect to the filter material surface or using a  
20 filter aid exhibiting a similar function can be used.

The process of the present invention further includes a step of dropwise adding, with stirring, the purified solution of coloring matter substance into a solution containing an amphoteric electrolyte in de-  
25 ionized water at a concentration of 10% or less to obtain a water-containing organic solvent solution containing said purified coloring matter substance and said amphoteric electrolyte (Step 3).

The de-ionized water used in this step preferably has an electrical conductivity of 5  $\mu$ S/cm or less.

The concentration of the coloring matter substance in the water-containing organic solvent solution obtained in this step is not particularly limited, but it can be varied depending on the applications. In the case of an ink for inkjet, the concentration is preferably 1-5 wt%.

10           The solution of the amphoteric electrolyte in the de-ionized water used in this step may be an aqueous solution obtained by merely dissolving an amphoteric electrolyte in de-ionized water, or in an aqueous solution containing a coloring matter substance  
15 and an amphoteric electrolyte obtained in Step 4 mentioned below or through Steps 4 and 5 mentioned below. That is to say, this step involves an aspect of dropwise adding the purified solution of coloring matter substance obtained in Step 2 into the aqueous  
20 solution of purified coloring matter substance and amphoteric electrolyte obtained by subjecting the water-containing organic solvent solution containing the purified coloring matter substance and amphoteric electrolyte obtained in this step to Step 4 or to Steps  
25 4 and 5 mentioned below, too. An advantage of this aspect lies in that Step 3 can be carried out always under the fixed dropping and dilution conditions, and as a result a stable concentrate solution can be

obtained.

As the amphoteric electrolyte used in this step, amino acids are preferred. Amino acids having an isoelectric point of 6 or above, namely arginine, histidine and glycine, are more preferred.

Further, as the amphoteric electrolyte usable in this step, in addition to the amino acids, oligomers, i.e. the low molecular weight products synthesized by the polymer synthesis and having a weight average molecular weight of 1,000 or less and therefore not classified as resin, such as amphoteric copolymers formed from hydrophobic monomers such as methacrylic acid, dimethylaminoethyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, other alkyl (meth)acrylates, styrene, etc. can also be used.

Next, Step 4 will be explained below.

This is a step for removing the organic solvent from the water-containing organic solvent solution comprising purified hydrophobic coloring matter substance and amphoteric electrolyte obtained in Step 3, to obtain an aqueous solution containing the coloring matter substance and the amphoteric electrolyte.

For this purpose, an azeotropic distillation of water and an organic solvent is carried out by the use of a distillation apparatus equipped with a temperature controlling device, a refluxing device, a pressure-reducing device and a stirring function,



optionally under a reduced pressure, to convert the system to a solution system of water only. Since the concentration rises with the progress of the step, de-ionized water and/or organic solvent can be

5 appropriately added in the course of the step, according to the need. This is a conventional technique of solvent substitution (phase conversion) with water well known to a person skilled in the art.

Since the solution thus obtained contains  
10 some quantity of coarse particles, the solution may be afterwards subjected to a high-speed centrifugation (Step 5). Although the number of rotation can be appropriately decided according to the coarseness, a preferable number of rotation is 5,000-15,000 rpm.

15 Thus, there can finally be obtained a colorant comprising water and said purified hydrophobic coloring matter substance reduced in the content of impurity electrolyte and coarse particle of coloring matter substance and containing said amphoteric  
20 electrolyte as essential ingredient.

Additionally speaking, the aqueous solution containing a coloring matter substance and an amphoteric electrolyte obtained in Step 4 or Steps 4 and 5 can be used as the aqueous solution containing  
25 amphoteric substance of Step 3, as has been mentioned above.

Next, the present invention will be explained in more detail with reference to examples.

Example 1

Step 1 and Step 2 in the present invention were carried out in the following manner. Firstly, a solution having the following formulation was dissolved  
5 at the ambient temperature using a four-necked 2 L flask equipped with a reflux condenser, a stirrer and a dropping funnel:

Blue coloring matter substance

SB 70 (VALIFAST BLUE 2606,

manufactured by Orient Kagaku) 25 parts by wt.

Isopropyl alcohol 475 parts by wt.

On the other hand, 50 parts by weight of a strong base-type anion exchange resin SA-20A (DIAION,  
10 manufactured by Mitsubishi Kagaku) previously activated into OH form and thoroughly washed, from which water was removed with a filter paper was prepared. After finely pulverizing the resin in a mortar, 25 parts by weight of the pulverized resin was taken and added to  
15 the above-mentioned solution. The mixture thus obtained was stirred at ambient temperature for 30 minutes. At this time, the powdery ion exchange resin had a granular size of 10-800  $\mu\text{m}$  as measured in water by means of CAPA 500 (optical particle size-measuring  
20 device manufactured by Horiba, Co., Ltd.).

Next, the solution obtained above was carefully filtered under a pressure of 0.2 mPa or less

with a filter material prepared by laying an industrial one-side flannel filter cloth on an industrial filter paper No. 126, to obtain a transparent colored solution.

5                   The solution thus obtained was divided into portions and introduced into a plurality of the same flasks. A portion of the solution in the first flask was dropwise added into a solution prepared by diluting a 9% aqueous solution of arginine with de-ionized  
10 water, under stirring. The resulting mixture was heated as it was, and distilled and concentrated under reduced pressure, and cooled. Next, another portion of the above-mentioned transparent colored solution was dropwise added to the concentrated and cooled solution  
15 obtained just above. By repeating the same procedure of concentrating the solution by distillation under reduced pressure and adding thereto the colored solution, an aqueous solution containing 5% of coloring matter substance was finally obtained. In total,  
20 dropping into an aqueous solution containing arginine only was carried out once, and dropping into the distilled aqueous solution containing the coloring matter substance and arginine was repeated three times. The over-all number of dropping was thus four. The  
25 content of the procedure, and the change of the properties of the liquid during the operation are summarized in Table 1.

Table 1

Step	No. of times of adding dye solution	1st	2nd	3rd	4th
	Solution number	(1)	(2)	(3)	(4)
Step 3	Dye solution (parts by wt.)	100	100	100	100
	De-ionized water, DIW (parts by wt.)	178			
	9% Aqueous solution of arginine (parts by wt.)	222			
	Used solution (1) (parts by wt.)		400		
	Used solution (2) (parts by wt.)			400	
	Used solution (3) (parts by wt.)				400
	Total	500	500	500	500
Step 4	Theoretical values after removal of IPA				
	Dye concentration	1.25%	2.50%	3.75%	5.00%
	Arg concentration	5.00%	5.00%	5.00%	5.00%
	Dye/Arg	1/4	2/4	3/4	4/4
	Properties after removal of IPA				
	Amount of removal (parts by wt.)	90.7	113.3	110.1	137.5
	Particle diameter D10%	0.015	0.020	0.026	0.037
	D50%	0.023	0.028	0.038	0.053
	D90%	0.051	0.070	0.158	0.151
	Nonvolatile residue (%)		7.74	9.72	13.30
	Centrifugation 11000 rmp × 10 min				
	D10%		0.015	0.020	0.025
	D50%		0.022	0.032	0.041
	D90%		0.044	0.059	0.085
	Nonvolatile residue (%)		7.42	9.17	12.45
	Yield		95.9%	94.3%	93.6%
	Characteristic properties				
	pH		10.93	10.77	10.72
	Conductivity (μs/cm)		523	800	1018
	Surface tension (mN/m)				41.6
	Viscosity (mPa·s)				
	50 rmp				2.94
	100 rmp				2.94

As shown in Table 1, there was obtained a colorant, namely a transparent colored solution, which was very fine and sharp in the particle size distribution, at high yield.

- 5                Similar processes to the above was carried out by using histidine and glycine in stead of arginine. The results obtained were similar to the above.

#### Example 2

- 10                The colorant obtained in Example 1 was compared with a commercially available inkjet ink of the same color, and their light-durabilities were measured.

- 15                Thus, each of the solutions was coated onto a hiding chart and exposed to the Fade-Ometer. The change in OD value was monitored. The results are shown in Table 2.

Table 2

	System	The present invention	Commercial product	Commercial product
	No.	(3)	Water-soluble dye system	Pigment system
	Coloring matter substance	SB-70		
	Dye concentration %	3.75		
	Amino acid concentration %	2.5		
OD	0	1.03	1.02	1.39
	1	1.03	1.01	1.38
	4	0.99	0.96	1.38
	7	0.97	0.88	1.35
	14	0.93	0.8	1.29
	0	100	100	100
Rate of change (%)	1	100.00	99.02	99.28
	4	96.12	94.12	99.28
	7	94.17	86.27	97.12
	14	90.29	78.43	92.81

The results shown in Table 2 demonstrate that the colorant of the present invention have light-durability comparable to that of pigment type colorants.

5 Example 3

On the Colorant (4) obtained in Example 1, a letter-printing test was carried out with a home-made testing machine using a commercially available printer. The results were as shown in Table 3.

10 The inking property was evaluated on a scale of one to five. An ink to be tested was introduced into an ink-cartridge of a commercially available printer. In the test, solid printing on 50 sheets of paper with the size of A4 was continuously carried out  
15 for each ink sample, and the printing property was evaluated based on continuous printability and the degree of thin spot generation. Specifically, the evaluation of printing property was based on the following criteria:

20 Five Points: Continuous printing on more than 50 sheets was achieved, without any thin spot;

Four Points: Continuous printing on more than 50 sheets was achieved, but with slight  
25 generation of thin spots;

Three Points: Continuous printing on more than 50 sheets was achieved, but with partial

generation of thin spots;

- Two points: Continuous printing was possible only on sheets less than 50 or significant number of thin spots were generated; and
- 5 One point: Printing was impossible.

Water resistance of the inks was also evaluated on a scale of one to five as follows. A solid printed matter was brushed back and forth on a printed surface for three times with a brush containing  
10 tap water, within 30 minutes after the solid printing. The states of the brush and the printed surface after the brushing were visually observed and evaluated based on the criteria:

- Five Points: No color fading was observed;
- 15 Four Points: Slight color fading on printed surface was observed;
- Three Points: Slight color fading on printed surface and coloration of brush were observed;
- Two Points: Significant color fading on printed  
20 surface and coloration of brush were observed; and
- One Point: Complete color fading on printed surface was observed.

Marring of the inks was evaluated on a scale  
25 of one to five as follows. A small piece of printing paper was placed onto a printed surface of the solid printing matter within 30 minutes after the solid printing. A load of 200 g/cm<sup>2</sup> was then applied onto the



piece and the piece was dragged on the printed surface with the load at a speed of 3 cm/sec. for a distance of 10 centimeters. Marring was evaluated based on the degree of color migration onto a part of the piece of printing paper contacted with the colored surface, based on the following criteria:

- Five points: No color migration was observed;
- Four points: Very slight color migration was observed;
- 10 Three points: Slight color migration was observed;
- Two points: Color migration and some color fading on printed surface were observed;
- One point: Color migration and color fading on printed surface were observed.

15 Storage stability of Colorant (4) was evaluated by storing Colorant (4) at 60°C and measuring the particle size distribution thereof one day, four days and seven days later. The results of the evaluation of storage stability are summarized in Table

Table 3

Ink formulation	The present invention	Commercially available water-soluble dye type ink
Example 1 colorant (4)	48.4	
IPA	3	
Diethylene glycol	10	
Glycerin	5	
DIW	33.5	
Total (parts by wt.)	100	
Filtering characteristic	0.8 $\mu$ m	
Properties	Membrane OK	
Particle diameter		
D10%	0.026	
D50%	0.042	
D90%	0.091	
Surface tension	38.0	28.9
Viscosity		
50 rpm	3.06	2.48
100 rpm	0.06	2.48
Inking property		
BC-30 Head (Black)		
Inking property	4	5
Dot diameter	80 $\mu$ m	
OD value *1		
Paper CP 250		
None	0.67	0.92
R	0.91	1.21
G	0.43	0.63
B	0.24	0.33
Glossy paper Sp 101		
None	0.75	
R	1.52	
G	0.37	
B	0.15	
Water resistance	3	1
Marring	5	5
BC-31 Head (Color)		
Inking property	1	5

\*1 OD value was measured with Macbeth concentration meter for transmission and reflection (Sakata Inks Co., Ltd., TR-927V).

None: visual (400-700  $\mu$ m filter); R: Red filter was used; G: Green-Red filter was used; B: Blue-Red filter was used.

Table 4

Example 1 colorant (4)

Characteristic properties	
Nonvolatile residue (%)	12.5
pH	
Viscosity 50 rpm	2.94
100 rpm	2.94
Particle diameter D10%	0.025
D50%	0.041
D90%	0.085
Conductivity ( $\mu\text{S}/\text{cm}$ )	1018
Surface tension ( $\text{mN}/\text{m}$ )	41.6
60°C Storage stability	
1 day later D10%	0.028
D50%	0.045
D90%	0.082
4 days later D10%	0.024
D50%	0.040
D90%	0.085
7 days later D10%	0.025
D50%	0.040
D90%	0.084

Thus, it was found that the dye type ink tested herein was sufficiently improved in water-durability, so that the ink was practically usable. It was also found that the colorant of the present  
5 invention is superior in storage stability.

#### Comparative Example 1

The process of Example 1 was repeated, except that Step 2 was omitted in one test and Step 3 was carried out without using the amphoteric electrolyte in  
10 the other test. The results are summarized in Table 5.

Table 5

		System without Step 2			System without amphoteric electrolyte
Step	No. of times of adding dye solution	1st time	2nd time 3rd time		1st time
	Solution number	H(1)	H(2)	H(3)	K(1)
Step 3	Phase change				
	Formulation				
	Dye solution	100	100	100	100
	DIW	178			400
	Alginine (q%)	222			0
	H(1)		400		0
	H(2)			400	0
	Total (parts by wt.)	500	500	500	500
Step 4	Theoretical values after removal of IPA				
	Dye concentration	1.25%	2.50%	3.75%	1.25%
	Arg concentration	5.00%	5.00%	5.00%	0.00%
	Dye/Arg	1/4	2/4	3/4	1/0
	Properties after removal of IPA				
	Amt. removed (parts by wt.)	89.2	104	105.6	100.2
	Particle size distribution D10%		0.033	0.063	0.053
	D50%		0.054	0.220	0.105
	D90%		0.142	2.393	0.327
	Nonvolatile residue (%)			8.3	1.13
Step 5	Centrifugation 11000 rmp × 10 min	Stopped due to the generation of coarse particles			
	D10%				0.0458
	D50%				0.0839
	D90%				0.1849
	Nonvolatile residue (%)				0.76
	Yield (Nonevolatile residue, %)				67.20%

The results of this example demonstrate the necessity of Step 2 and the necessity of the amphoteric electrolyte.

According to the present invention, a method  
5 for providing a colorant for inkjet inks which is high  
in light-durability and low in price was accomplished.  
Accordingly, the present invention much contributes to  
production processes of the existing colorants in this  
field and the colorants expected to be developed in the  
10 future.